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# MODULATED MOLECULAR BEAM STUDY OF THE SURFACE MEDIATED RECOMBINATION REACTION:

## $O\ (1.5\ eV) + NO \rightarrow NO_2$
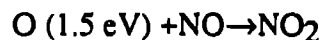
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## Abstract

The surface mediated recombination of hyperthermal (1.5 eV) atomic oxygen and NO on sapphire ($Al_2O_3$) to form $NO_2$ has been studied using mass spectrometric detection of the $NO_2$. The signal amplitude at M/e=46 ($NO_2^+$) is sensitive to the sapphire substrate temperature ($T_s$) with the signal maximizing at $T_s \sim -30$ °C and lower at $T_s \sim +40$ and -55 °C. Modulation of the hyperthermal atomic oxygen beam produces a modulation in the $NO_2$ signal which correlates with the photon component of the beam and has a time constant of 0.4 milliseconds over a modulation frequency range of 100-400 Hz at a substrate temperature of -30 °C. It is concluded that the $NO_2$ heat of adsorbtion on sapphire is ~0.65 eV and photodesorbs from the surface.

## 1. Introduction

A visible glow above Shuttle surfaces facing the ram direction (direction of travel) was first observed on the STS-3 mission and reported by [Banks et al., 1983). Mende and coworkers characterized the glow [Mende et al., 1988 and references there in] which peaked at 680 nm and correlated with a slightly red shifted $NO_2$ spectra. A number of authors, [Torr et al., 1979; Swenson et al., 1985; Kofsky and Barrett, 1986], then suggested that recombination of nitrogen atom produced NO with excess O might be the source of the chemiluminescence. Several investigators [Arnold et al., 1988; Caledonia et al., 1990] undertook chemiluminescence laboratory studies of the O+NO reaction mediated by surfaces of nickel, aluminum, and Z306 Chemglaze[(R)] paint using photomultiplier tube detectors. Both studies found spectra which showed qualitative agreement with Shuttle based studies. We report here a study of the O+NO surface mediated recombination reaction which uses mass spectrometric detection of the reaction products and thus measures the sum of radiative and nonradiative $NO_2$ molecules produced.

## 2. Experimental

Hyperthermal atomic oxygen is produced via a cw laser sustained plasma technique

[Cross et al., 1989] having a variable translational energy range of 1-5 eV. This study used a 10%$O_2$ in Argon gas mixture which produced a beam kinetic energy of 1.5 eV with ~90% dissociation into atomic oxygen. While the apparatus has been described in detail previously [Cross et al., 1989], Figure 1 shows an addition to the primary apparatus in which a quadrupole residual gas analyzer is employed to measure both the intensity and temporal profile of the direct beam and the surface scattered beam and reaction products. The direct beam measurement is made by retracting the solid sample and swinging the residual gas analyzer into the sample position. The atomic oxygen flux in this portion of the apparatus which is 1.25 meters from the atomic oxygen source is 2-5 X $10^{14}$ AO/s-cm$^2$. A precision leak valve is used to control the NO partial pressure (5X$10^{-7}$ torr) in the chamber. An average NO flux at the sample surface is estimated to be ~5X$10^{15}$ NO/s-cm$^2$. The sample is presently radiation cooled by the liquid nitrogen shroud with no active temperature control, though a heater on the sample manipulator is used to bake and clean the sapphire before cooling.

A variable speed hysteresis motor is used to drive the molecular beam chopper wheel while a lamp/photocell combination is used to monitor the chopper frequency and provide a reference signal for the pulse counting multichannel scaler data acquisition unit. A photomultiplier tube with a S-20 photocathode and a narrow band pass filter centered at 3200Å is used to detect the prompt modulated photon signal from the atomic oxygen source plasma region.
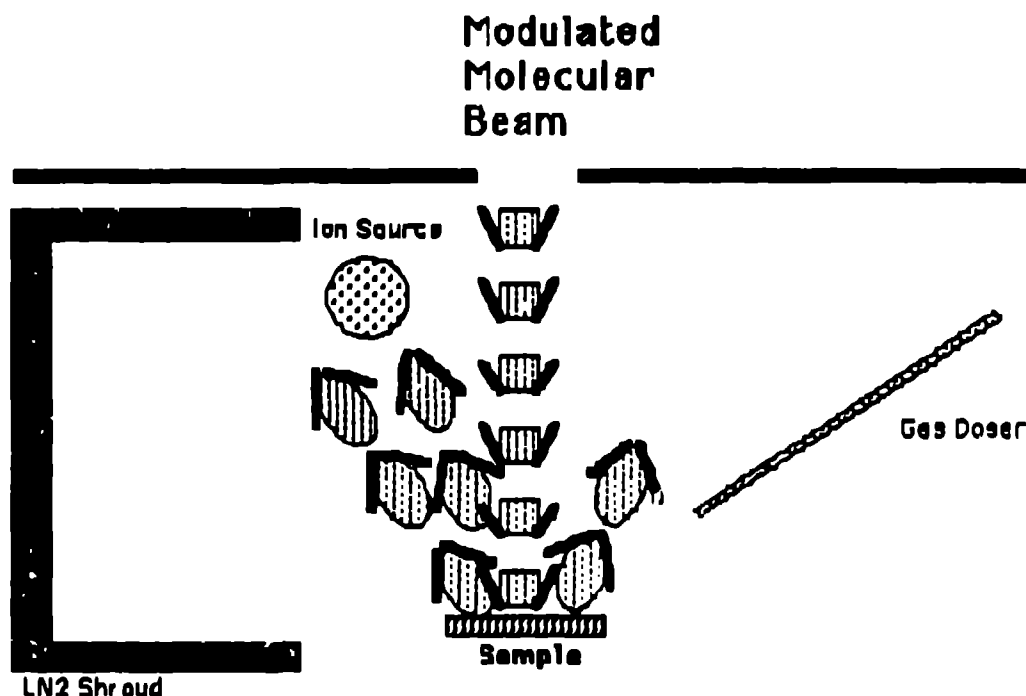


Figure 1. Modulated beam detector assembly showing the residual gas analyzer ion source with the residual gas analyzer perpendicular to the figure. A gas doser consisting of a 1/8" diameter copper tube is placed 4 cm from the sample surface.

## 3. Results

Figure 2 shows the scattered $O_2$ modulated signal recorded at 400 Hz (a) and 100 Hz (b) modulation frequencies. In both cases the dashed (----) line shows the fit to the direct atomic oxygen modulation signal while the solid line is the best fit to the M/e=32 scattered signal when the sapphire sample temperature was -55°C (a) and -24°C (b). Note that the modulated scattered signal correlates with the atomic oxygen direct beam and not the photon component of the beam. A double exponential (1) was found to fit the data

$$fit=exp(-t/\tau_1)+c \cdot exp(t/\tau_2) \qquad (1)$$

where $\tau_1$ and $\tau_2$ are time constants and $c/(1+c)$ is the fractional component of $\tau_2$. The data at 400 Hz in Figure 2a ($T_s$=-55°C) is fit with $c=\tau_2=0$ and $\tau_1=50$ $\mu$s where as the data at 100 Hz in Figure 2b (Ts=-24°C) is fit with $\tau_1=0.4$ ms,c=0.5, and $\tau_2=40$ ms.
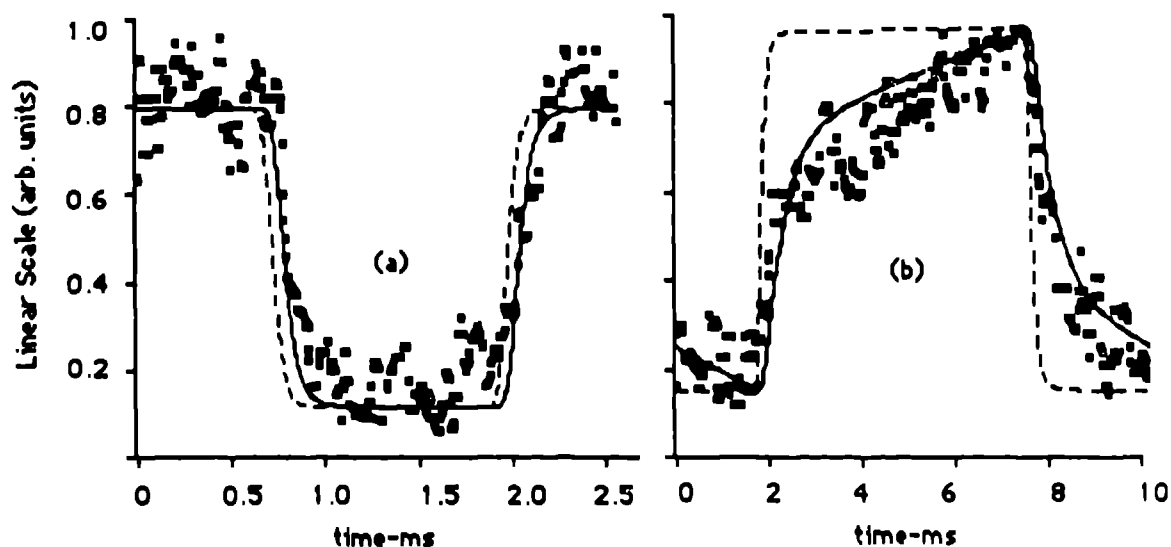


Figure 2. Scattered modulated $O_2$ from sa_ phire at 400Hz, Ts=-55° C (a) and 100 Hz, Ts=-24°C (b), $\tau_{1a}$=50$\mu$s and $\tau_{1b}$=0.4 ms, $\tau_{2b}$=40 ms, and c=0.5 (see equation 1). The dashed line (---) is the direct atomic oxygen beam waveform.

Note that two exponentials are needed to fit the low frequency, high temperature data while only one is needed to fit the high frequency, low temperature data. The ratio of modulated to DC intensity is 0.02 at 400 Hz and 0.09 at 100 Hz.

Figure 3 shows the modulated data for $NO_2$ desorbing from sapphire at 400 Hz, $T_s$=-30 °C (a) and 100 Hz, $T_s$=-55 °C (b). A single time constant of 0.4 ms fits both modulation frequencies making c and $\tau_2$ equal to zero. The dashed line shows the modulated photon signal produced by the atomic oxygen plasma. Note that the $NO_2$ desorption correlates with the photon modulation and not the atomic oxygen modulation as in the case of $O_2$ scattering in Figure 2. The ratio of modulated signal to unmodulated signal is 0.45 at 400 Hz and 0.62 at 100 Hz. The total intensity (modulated+DC) is temperature dependent and maximizes between -30 °C to     (     At -55 °C and +40 °C the intensity is ≈20% that of the maximum. Several tests were made to insure that the

$NO_2$ is not originating from $NO_2$ in the NO bottle or from gas phase reactions. First, the absolute $NO_2$ intensity rose by a factor of ~3 when NO is introduced into the vacuum chamber with the atomic oxygen beam off as compared to a factor of 30 with the sample in the atomic oxygen beam. Secondly, irradiation of cold sapphire by a 3 eV translational energy pure argon beam with simultaneous NO dosing produced no measurable signal. Thirdly, removing the sapphire from the beam reduced the $NO_2$ intensity by a factor of ~30. We conclude from these facts that the $NO_2$ is indeed being produced on the sapphire surface and not else where in the detector system.
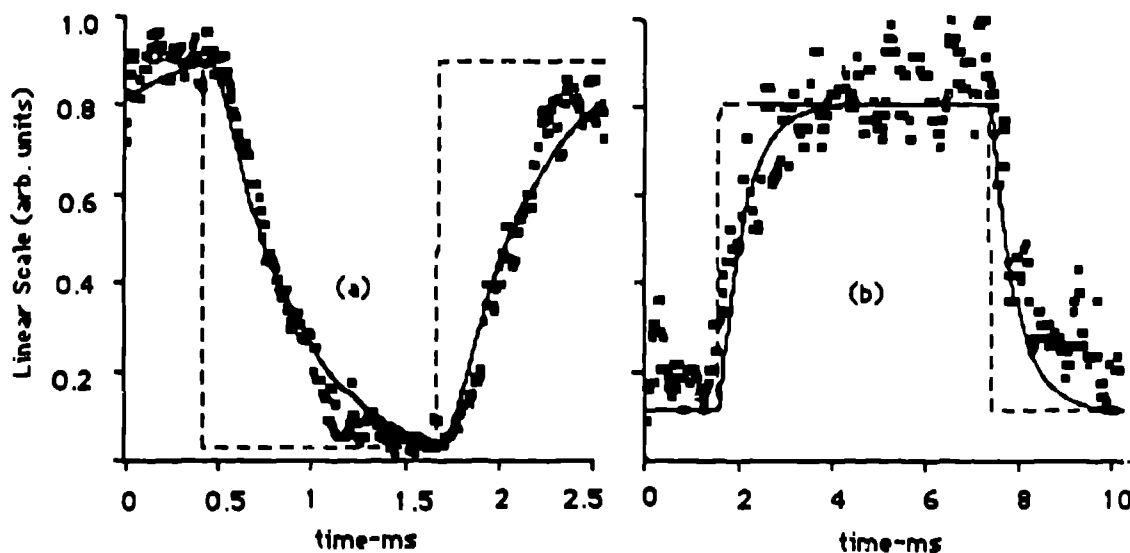


Figure 3. Modulated $NO_2$ desorption from sapphire at 400 Hz, $T_s$=-30 °C (a) and 100 Hz, $T_s$=-55 °C (b). Only a single time constant of 0.4 ms is needed to fit both cases. Note that the dashed line(---) is the direct beam photon waveform.

## 4. Discussion

The modulation spectra shown in Figure 2 of $O_2$ scattering/desorption indicate that a fairly complicated process is occurring which leads to modulation of the $O_2$. The ratio of modulated to DC signal as well as the shape of the modulated waveform are a strong function of chopping frequency. At a high chopping frequency direct process are occurring such as scattering of $O_2$ from the direct beam, while at a low chopping frequency recombination and subsequent desorption can occur. We will not address these very interesting phenomena in this paper but rather concentrate on the $NO_2$ production.

The $NO_2$ modulated waveform is describable using only a single exponential which correlates with the photon component of the beam. That is the desorbtion of $NO_2$ from the surface is independent of when the atomic oxygen strikes the surface indicating that the heat of adsorbtion is high and therefore the desorbtio1 is slow compared to the modulation frequencies used in this investigation. The $NO_2$ intensity does go to zero though when the beam is flagged but it takes on the order of 30 seconds for this to occur which is fast compared to the cooling time for the sample (~20 minutes). This long

desorbtion time constant corresponds to a heat of adsorbtion of 14.9 kcal/mole (equation 2 [Somorjai, 1972]).

$$\tau_{des}=10^{-12}exp[\Delta H_{ads}/RT] \hspace{3cm} (2)$$

The photon induced desorbtion can be caused by either heating of the surface or direct excitation of the vibrational or electronic modes of $NO_2$. Separate investigations using thin film platinum resistance thermometers deposited on sapphire substrates indicate that no more than a 5 °C temperature rise due to thermal heating would be expected. This amount of thermal heating is not sufficient to explain the 0.4 ms photon induced desorbtion time constant. The effective temperature required to produce a desorbtion time constant of 0.4 ms with a 14.9 kcal/mole heat of adsorption is 380 K. This is not an unreasonable temperature to achive as the photon component of the beam has an appreciable UV and visible component [Cross, et al., 1989] which would be capable of exciting internal modes of $NO_2$ [Okabe, 1978] resulting in a localized high temperature region from which $NO_2$ could photodesorb. It is also interesting to note that collisional desorbtion due to 3 eV argon which would correlate with the atomic oxygen modulation is not observed even though the collision energy is over 4 times the heat of adsorbtion.

In summary we have shown through mass spectrometric detection that surface mediated recombination of O+NO leads to $NO_2$ which is bound to sapphire through a heat of adsorption of 0.65 eV. We have not measured the excited state (visible luminescence) to ground state ratio but we have shown that the $NO_2$ produced under these conditions photodesorbs under conditions where the thermally induced temperature rise of the surface is <5 °C which is insufficient to explain the desorbtion. desorb

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